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(54) LIQUID CLEANER COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a liquid cleaner composition excellent in foaming force, activities for lowering the oil/water interface tension while maintaining the low temperature stability excellent.

SOLUTION: This liquid cleaner composition comprises (a) 0.5-20 wt.% compound of the formula; RO-(EO)x-(PO)y-(EO)x'-H [R is an 8-22C alkyl group, etc.; EO is an oxyethylene group; PO is an oxypropylene group; (x) and (x') are each a number of ≥1, with the proviso that the sum of (x) and (x') is 4-20; (y) is a number of 0.5-6; with the proviso that (EO)x, (PO)y, and (EO)x', forms block bonds in the order], (b) 1-50 wt.% sulfate type or sulfonate type anionic surfactant and, (c) 0.1-10 wt.% ampholytic, amine oxide-based or fatty acid diethanolamide-based surfactant.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the liquid cleaning agent constituent which is excellent in the foam formation force, and an oil / water boundary tension fall ability, maintaining freeze thaw stability good in detail about a liquid cleaning agent constituent.

[0002]

[Description of the Prior Art] A detergency and the foam formation force are mentioned as most fundamental performance for which a cleaning agent constituent for home use is asked. It is said that there is generally no relevance universal between a detergency and the foam formation force. However, a consumer is in the inclination which likes foaming rich also from the point of acceptability judging a detergency in many cases with disappearance of a bubble at the time of washing. For this reason, as goods, the foam formation force, especially the cleaning agent which has rich foaming also under oil dirt existence are desirable.

[0003] The conventional cleaning agent mainly makes an anionic surface active agent the main washing basis from the reason of the foam formation force, it is the purpose of relief of the operation to the foam formation force reinforcement under oil dirt existence, and the skin further, and nitrogen-containing both sexes, such as tertiary amine oxide, a higher-fatty-acid alkanol amide, and an alkyl betaine, cation nature, or the nonionic surfactant is used together. However, in the cleaning agent constituent by the combination of these surfactants, generally, on the surface chemistry-property of a surfactant, it is in the inclination for the foam formation force to be spoiled, so that the emulsification force over fats-and-oils dirt becomes high.

[0004] Moreover, a sulfate type or a sulfonate type anionic surface active agent is a surfactant with the outstanding detergency and the outstanding foam formation force, and has been widely used as a raw material of a liquid cleaning agent. however, since the freeze thaw stability of a compound is bad, glycols, such as low-grade alkylbenzene sulfonates, such as lower alcohols, such as ethanol, a benzenesulfonic-acid salt, and a p-toluenesulfonic-acid salt, ethylene glycol, and a propylene glycol, a urea, etc. are independent as a low-temperature stabilizing agent -- or it has been combined and used By a urea showing the outstanding effect in these, since it is economical, although used widely, it decomposes, when saved at an elevated temperature, and unpleasant smell, such as an ammonia smell, is generated or there is a fault which raises pH. On the other hand, if other low-temperature stabilizing agents are little, even if they have few effects and carry out abundant combination, sufficient low-temperature stabilization effect accepts and is uneconomical [stabilizing agents].

[0005] Then, although to use together with the alcoholic ethoxy rate system nonionic surface active agent which has a detergency as a surfactant and has a low-temperature stabilization effect had been tried, when the low-temperature stabilization effect was blended yet fully and so much, it had the fault to which washing nature and foamability also fall.

[0006] Therefore, the purpose of this invention is to offer the cleaning agent constituent which is excellent in the foam formation force, and an oil / water boundary tension fall ability, maintaining freeze thaw stability good.

[0007]

[Means for Solving the Problem] As a result of inquiring wholeheartedly, by blending the block copolymer of 3 yuan with the specific number of alkylene oxide addition mols and a specific addition form, this invention persons find out that the above-mentioned technical problem is solvable, and came to complete this invention. That is, this invention is following (a). A component and (b) A component and (c) The liquid cleaning agent constituent characterized by containing a component is offered.

[0008] (a) Compound RO-(EO)x-(PO) y-(EO)x' expressed with a general formula (I) - H (I)
R shows the alkyl group or ARUKENIRU machine of the straight chain of carbon numbers 8-22, or branched chain among [formula, EO shows an oxyethylene machine and PO shows an oxypropylene machine. x and x' is one or more numbers which show the number of average addition mols of an ethyleneoxide, and the sums of x and x' are 4-20. y It is the number of 0.5-6 which shows the number of average addition mols of ** propylene oxide. In addition, x, (PO) y, and (EO)x' are carrying out block combination at this order.]

(b) A sulfate type or sulfonate type anionic surface active agent (c) An amphoteric surface active agent, an amine oxide system surfactant, or fatty-acid diethanolamide system surfactant. [0009]

[Embodiments of the Invention] Hereafter, the form of operation of this invention is explained in detail.

[0010] [(a) Component] Cleaning agent constituent of this invention The compound expressed with the above-mentioned general formula (I) as a (a) component is contained. The compound expressed with a general formula (I) is a general formula (II).

· R-OH (II)

(-- R shows the aforementioned meaning among a formula It can obtain by the ethyleneoxide to the alcohol expressed with), and, next, can obtain propylene oxide and by making order carry out block addition of the ethyleneoxide further.

[0011] As alcohol expressed with a general formula (II) The alcohol of the straight chain, the saturation of 10-14 or an unsaturation, of the 1st class or the 2nd class or a branched chain is mentioned preferably. carbon numbers 8-22 -- as a concrete example Linear alcohols, such as decyl alcohol, lauryl alcohol, a myristyl alcohol, and a stearyl alcohol, The mixed alcohol mixed in the range of carbon numbers 8-22, the alcohol of the carbon numbers 8-22 which have branching compounded using the oxo process or the Ziegler process, etc. are mentioned, and especially lauryl alcohol is desirable.

[0012] Moreover, although the method of adding to these alcohol under existence of a catalyst using the alkoxyl-ized method well-known as a method of adding alkylene oxide is mentioned, the addition sequence of alkylene oxide needs to add an ethyleneoxide first, next needs to add propylene oxide, and needs to carry out block addition of the ethyleneoxide further at order. If an ethyleneoxide and propylene oxide are made to add at random, foaming will be checked and it is not desirable.

[0013] The sum total ($x+x'$) of the number of average addition mols of the ethyleneoxide of a compound expressed with the general formula (I) of this invention is four mols or more 20 mols or less, and is five mols or more eight mols or less preferably. The compatibility of the compound and water which are expressed with a general formula (I) that the sum total of the number of average addition mols of an ethyleneoxide is less than four mols becomes bad, and handling nature will become bad if it exceeds 20 mols.

[0014] Moreover, the number y of average addition mols of the propylene oxide of the compound expressed with a general formula (I) It is 0.5 mols or more six mols or less, and two mols or more four mols or less are desirable, and especially two mols are desirable. The number of average addition mols of propylene oxide In not fulfilling 0.5 mols, change of viscosity is large, handling nature gets worse, and if the amount exceeding six mols is added, a detergency will decline.

[0015] (a) in the cleaning agent constituent of this invention The content of a component has 0.5 - 20 desirable % of the weight, and its 1 - 10 % of the weight is still more desirable.

[0016] [(b) Component] Cleaning agent constituent of this invention As a (b) component, a sulfate type or a sulfonate type anionic surface active agent is contained. As the sulfate type used for this invention, or a sulfonate type anionic surface active agent, it is the following (i), for example. - (v) One sort chosen from a group or two sorts or more are mentioned.

[0017] (i) the carbon number of an alkyl group -- 9-15 -- desirable -- 11-14 -- especially -- desirable -- straight chain alkylbenzene sulfonates (ii) of 12 Carbon numbers 8-22 and by sulfuring the alcohol of 12-16 preferably alkyl sulfate (iii) obtained carbon numbers 8-22 -- desirable -- alkane sulfonate (iv) of 12-16 carbon numbers 8-22 -- desirable -- alpha-olefin sulfonate (v) of 12-16 carbon numbers 8-22 -- preferably the alcohol of 12-16 the polyoxyethylene-alkyl-ether sulfate guided by ethoxylating by 1-12 mols preferably 1-30 mols of ethyleneoxides -- (b) of these Among components In respect of a detergency and skin mild nature, a polyoxyethylene-alkyl-ether sulfate, General formula (III) $R_1O(CH_2CH_2O)_mSO_3M$ of especially a degree (III) (R_1 shows the alkyl group or alkenyl machine of carbon numbers 12-16 among a formula, M shows alkali metal, ammonium, or an alkanolamine, and m shows the number of 1-12 on an average.) The polyoxyethylene-alkyl-ether sulfate expressed is desirable.

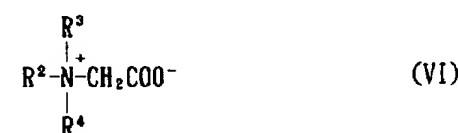
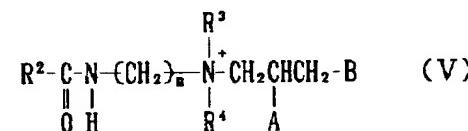
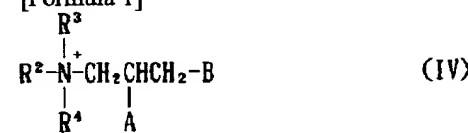
[0018] (b) in the cleaning agent constituent of this invention The content of a component has 1 - 50 desirable % of the weight, and its 5 - 30 % of the weight is still more desirable.

[0019] [(c) Component] The cleaning agent constituent of this invention is (c), in order to raise the foam formation force and to make the operation to the skin improve. An amphoteric surface active agent, an amine oxide system surfactant, or a fatty-acid diethanolamide system surfactant is contained as a component.

[0020] As an amphoteric surface active agent used for this invention, it is the following general formula. (IV) - (VI) The alkyl carbobetaine expressed and alkyl sulfobetaine are mentioned.

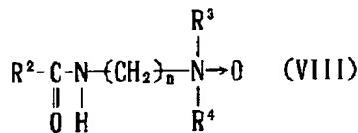
[0021]

[Formula 1]



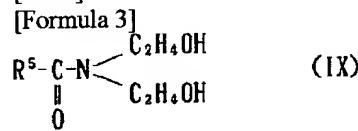
- [0022] (R₂ shows the alkyl or alkenyl machine of carbon numbers 8-22 among a formula, R₃ and R₄ show independently the alkyl group of carbon numbers 1-3, respectively, A shows a hydrogen atom or a hydroxyl group, B shows -COO- or -SO₃-, and n shows the integer of 1-5.)
Moreover, as an amine oxide system surfactant used for this invention, it is the following general formula (VII). Or (VIII) the tertiary amine oxide expressed is mentioned.

[0023]
[Formula 2]



- [0024] (R₂, R₃, and R₄ and n show the aforementioned meaning among a formula.)
Moreover, as a fatty-acid diethanolamide system surfactant used for this invention, the compound expressed with the following general formula (IX) is mentioned.

[0025]

 $\text{C}_2\text{H}_4\text{OH}$

- [0026] (R₅CO- shows the saturation or the unsaturated fatty acid residue of carbon numbers 10-20 among a formula.)
It sets to a general formula (IX) and is R₅CO-. As a fatty-acid residue shown, the residue of fatty acids, such as a lauric acid, a myristic acid, a palmitic acid, oleic acid, stearin acid, isostearic acid, palm oil fatty acid, a palm-kernel-oil fatty acid, a beef tallow fatty acid, a castor oil fatty acid, and a rapeseed-oil fatty acid, is mentioned, and a lauric acid, palm oil fatty acid, and a palm-kernel-oil fatty acid are desirable in these.

- [0027] (c) in the cleaning agent constituent of this invention The content of a component has 0.1 - 10 desirable % of the weight, and its 1 - 8 % of the weight is still more desirable.

[0028] Although the remainder of the aforementioned component of the cleaning agent constituent of this invention is water, nonionic surface active agents, such as fatty acid alkanolamide other than a sulfate type or anionic surface active agents other than sulfonate type anion surface activity, and fatty-acid diethanolamide, can be included. Furthermore, low-grade alkylbenzene sulfonates, such as glycols, such as lower alcohols like a well-known low-temperature stabilizer, for example, ethanol, and an isopropanol before, ethylene glycol, a polyethylene glycol, a propylene glycol, and a polypropylene glycol, a benzenesulfonic-acid salt, a p-toluenesulfonic-acid salt, and a xylene sulfonate, acetamides, and the aromatic carboxylates like a benzoate or a salicylate can be used together. In addition, many well-known matter can already be suitably used together according to the purpose as what can be blended with a liquid cleaning agent. As such matter, additives, such as a hand dry-area inhibitor, an enzyme, a germicide, an antimicrobial agent, a protein derivative, opaquer, a colorant, preservatives, perfume, a bleaching agent, a rusr-proofer, and a chelating agent, are mentioned to the organic builder and the inorganic builder for raising the detergency of a citric acid, a malic acid, a gluconic acid, or its salt, and a pan.

[0029] Although the cleaning agent constituent of this invention is suitably used as hard surface washing agents, such as a cleaning agent for kitchens, a cleaning agent for dwellings, and metal plastics, the cleaning agent for garments, the cleaning agent for hair, a cleaning agent for the bodies, etc., it is desirable to use as a cleaning agent for kitchens especially.

[0030]

[Example] Although an example is given and the cleaning agent constituent of this invention is explained in more detail hereafter, this invention is not limited to these examples. The section in an example and % are weight criteria unless it mentions specially.

[0031] In addition, (a) used in the example The component was compounded by changing an addition under the following conditions according to the number of addition mols of each ethyleneoxide or propylene oxide. Synthetic conditions are shown below. an ethyleneoxide -- ** -- a propylene -- oxide -- ** -- two -- a ** -- measurement -- a tub -- having been attached -- five -- ml -- rotation -- stirring -- a formula -- an autoclave -- inside -- lauryl alcohol -- [-- " -- a tradename -- a cull -- a call -- 2098 -- " -- Kao -- Co., Ltd. -- make --] -- 500 -- g -- a potassium hydroxide -- 3.0 -- g -- teaching -- a nitrogen purge -- having carried out -- after -- 110 ** -- a temperature up -- carrying out -- 40 Until next carry out a temperature up to 150 **, it introduces into an autoclave the ethyleneoxide [the amount which is equivalent to x of a general formula (I)] of the amount corresponding to the target compound by the pressure of 3.5 kg/m², a pressure declines and it becomes fixed. It was made to react until cooled to 120 **, it introduced into an autoclave the propylene oxide [the amount which is equivalent to y of a general formula (I)] of the

amount corresponding to the target compound by the pressure of 3.5 kg/m², a pressure declined and it became fixed, after making it react. Then, it was made to react until it became fixed, and a pressure declines, temperature was reduced [the temperature up was again carried out to 150 **, the ethyleneoxide [the amount which is equivalent to x' of a general formula (I)] was introduced into the autoclave by the pressure of 3.5 kg/m²,] after the reaction end, and the last target product was obtained by adding acetic-acid 3.2 g and neutralizing.

[0032] (a) which prepares the base compound shown in one to examples 1-6 and example of comparison 4 Table 1 and 2, and is shown in Table 1 and 2 at this base compound It added at a rate which shows a component or (a') a component in Table 1 and 2, and the cleaning agent constituent was prepared. An oil / the water boundary tension fall effect, the **** effect, the Krafft point fall effect, and the oil dirt detergency were evaluated by the following method about the obtained cleaning agent constituent. A result is shown in Table 1 and 2.

[0033] The boundary tension of the interface of the liquid and water which diluted an oil / <water boundary tension fall effect> each constituent with water 40 times was measured by Wilhelmy plating method (25 degrees C), and the effect was judged on the following criteria. In addition, the value in the liquid which diluted the base compound with water 40 times was made into the reference value.

Criterion +: - to which the measured value in low **:each constituent does not change the measured value in each constituent with a reference value rather than a reference value: The measured value in each constituent is higher than a reference value.

[0034] The <**** effect> cleaning agent constituent concentration After putting 40ml (use water is water of German hardness 3.5 degreeDH) of 0.2% of detergent solutions into the glass cylinder with a diameter of 5cm and stirring by the moving vane, bubble height was measured and it judged on the following criteria. In addition, the value in a base compound was made into the reference value.

Criterion +: - which does not change the measured value in **:each constituent with the measured value higher than a reference value in each constituent with a reference value: The measured value in each constituent is a low from a reference value.

[0035] The Krafft point of <Krafft point fall effect> each constituent was measured, and the effect was judged on the following criteria. In addition, the value in a base compound was made into the reference value.

-:<oil dirt detergency> beef tallow to which the measured value in low **:each constituent does not change the measured value in --:each constituent with a reference value rather than a reference value -- as an indicator -- Sudan III (red dyes) -- 0.1 % addition -- carrying out -- this -- 2.5g was applied to the pan made from ** (diameter of 25cm). [with the measured value higher than a reference value in each constituent] Using the sponge into which the solution which dissolved 3g of cleaning agent constituents for this in 27g (degree-of-hardness 3.5 degreeDH) of water was infiltrated, it rubbed, washed and carried out and beef tallow expressed the detergency with 20 degrees C of solution temperature with the number of sheets of the pan which was fully able to be washed and removed.

[0036]

[Table 1]

		実施例						
		1	2	3	4	5	6	
液体洗浄剤組成物	ベニス配合物	対オキシエレン(HO=3)ラウリルエーテルサルファート	18	18	18		18	15
		α -オレフィン(C_{14})スルホネート				12		
		ラウリルジメチルアミノキサイド	7	7	7	3		
		N-(3-フェタノイルアミドプロピル)-N-ジメチルアンモニオカムキシペタイン				3		
		バーム核油脂肪酸ジエタノールアミド					7	
		エタノール	5	5	5	5	5	
		イオン交換水	65	65	65	75	68	
(部)	(a) 成分	R=C ₁₂ H ₂₅ x=2、y=2、x'=3	5				5	
		R=C ₁₂ H ₂₅ x=3、y=2、x'=3		5		5		
		R=C ₁₂ H ₂₅ x=2、y=2、x'=5			5		5	
	(a') 成分	R=C ₁₂ H ₂₅ x=0、y=2、x'=3						
		R=C ₁₂ H ₂₅ x=0、y=0、x'=6						
pH			7	7	7	7	7	
結果	評価	油／水界面強力低下効果	+	+	+	+	+	
		増泡効果	+	+	+	+	+	
		クラフト点低下効果	+	+	+	+	+	
	油汚れ洗浄力	(枚数)	10	10	10	9	9	

[0037]
[Table 2]

		比較例				
		1	2	3	4	
液体洗浄剤	ベニス配合物	エチオキシジメチレン(EO=3)ラウリルエーテルアミドフェート α -オレフィン(C ₁₄)スルホネート	18	18		18
		ラウリルジメチルアミノキサイド	7	7	3	
		N-(3-ドデカノイルアミドプロピル)-N,N-ブチルアンモニオカルボキシペイント				
		バーム状油脂脂肪酸ジエタノールアミド				
		エタノール	5	5	5	5
		イオン交換水	65	65	87	72
組成物	(a) 成分 ^{*1}	R=C ₁₂ H ₂₅ x=2, y=2, x'=3				
		R=C ₁₂ H ₂₅ x=3, y=2, x'=3			5	
		R=C ₁₂ H ₂₅ x=2, y=2, x'=5				5
	(a') 成分 ^{*2}	R=C ₁₂ H ₂₅ x=0, y=2, x'=3	5			
		R=C ₁₂ H ₂₅ x=0, y=0, x'=6		5		
	pH		7	7	7	7
評価結果	油／水界面強力低下効果	+	-	-	-	
	増泡効果	-	+	-	-	
	クラフト点低下効果	+	+	+	+	
	油汚れ洗浄力 (枚数)	7	7	2	3	

[0038] Notes

*1: R in the compound expressed with a general formula (I), x, y, and x' A value shows.

[0039] *2: (a) R in the comparison article of a component, and the compound expressed with a general formula (I), x, y, and x' A value shows.

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[0004] Moreover, a sulfate type or a sulfonate type anionic surface active agent is a surfactant with the outstanding detergency and the outstanding foam formation force, and has been widely used as a raw material of a liquid cleaning agent. however, since the freeze thaw stability of a compound is bad, glycols, such as low-grade alkylbenzene sulfonates, such as lower alcohols, such as ethanol, a benzenesulfonic-acid salt, and a p-toluenesulfonic-acid salt, ethylene glycol, and a propylene glycol, a urea, etc. are independent as a low-temperature stabilizing agent -- or it has been combined and used By a urea showing the outstanding effect in these, since it is economical, although used widely, it decomposes, when saved at an elevated temperature, and unpleasant smell, such as an ammonia smell, is generated or there is a fault which raises pH. On the other hand, if other low-temperature stabilizing agents are little, even if they have few effects and carry out abundant combination, sufficient low-temperature stabilization effect accepts and is uneconomical [stabilizing agents].

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MEANS

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If an ethyleneoxide and propylene oxide are made to add at random, foaming will be checked and it is not desirable.
[0013] The sum total ($x+x'$) of the number of average addition mols of the ethyleneoxide of a compound expressed with the general formula (I) of this invention is four mols or more 20 mols or less, and is five mols or more eight mols or less preferably. The compatibility of the compound and water which are expressed with a general formula (I) that the sum total of the number of average addition mols of an ethyleneoxide is less than four mols becomes bad, and handling nature will become bad if it exceeds 20 mols.

[0014] Moreover, the number y of average addition mols of the propylene oxide of the compound expressed with a general formula (I) It is 0.5 mols or more six mols or less, and two mols or more four mols or less are desirable, and especially two mols are desirable. The number of average addition mols of propylene oxide In not fulfilling 0.5 mols, change of viscosity is large, handling nature gets worse, and if the amount exceeding six mols is added, a detergency will decline.

[0015] (a) in the cleaning agent constituent of this invention The content of a component has 0.5 - 20 desirable % of the weight, and its 1 - 10 % of the weight is still more desirable.

[0016] [(b) Component] Cleaning agent constituent of this invention As a (b) component, a sulfate type or a sulfonate type anionic surface active agent is contained. As the sulfate type used for this invention, or a sulfonate type anionic surface active agent, it is the following (i), for example. - (v) One sort chosen from a group or two sorts or more are mentioned.

[0017] (i) the carbon number of an alkyl group -- 9-15 -- desirable -- 11-14 -- especially -- desirable -- straight chain alkylbenzene sulfonates (ii) of 12 Carbon numbers 8-22 and by sulfurating the alcohol of 12-16 preferably alkyl sulfate (iii) obtained carbon numbers 8-22 -- desirable -- alkane sulfonate (iv) of 12-16 carbon numbers 8-22 -- desirable -- alpha-olefin sulfonate (v) of 12-16 carbon numbers 8-22 -- preferably the alcohol of 12-16 the polyoxyethylene-alkyl-ether sulfate guided by ethoxylating by 1-12 mols preferably 1-30 mols of ethyleneoxides -- (b) of these Among components In respect of a detergency and skin mild nature, a polyoxyethylene-alkyl-ether sulfate, General formula (III) R1O(CH₂CH₂O) m SO₃M of especially a

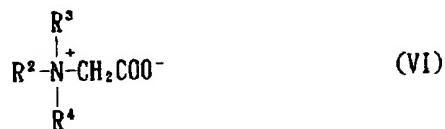
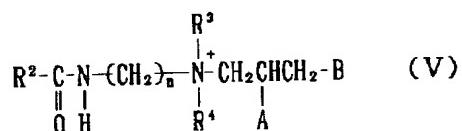
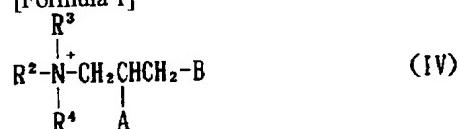
degree (III) (R1 shows the alkyl group or alkenyl machine of carbon numbers 12-16 among a formula, M shows alkali metal, ammonium, or an alkanolamine, and m shows the number of 1-12 on an average.) The polyoxyethylene-alkyl-ether sulfate expressed is desirable.
 [0018] (b) in the cleaning agent constituent of this invention The content of a component has 1 - 50 desirable % of the weight, and its 5 - 30 % of the weight is still more desirable.

[0019] [(c) Component] The cleaning agent constituent of this invention is (c), in order to raise the foam formation force and to make the operation to the skin improve. An amphoteric surface active agent, an amine oxide system surfactant, or a fatty-acid diethanolamide system surfactant is contained as a component.

[0020] As an amphoteric surface active agent used for this invention, it is the following general formula. (IV) - (VI) The alkyl carbobetaine expressed and alkyl sulfobetaine are mentioned.

[0021]

[Formula 1]

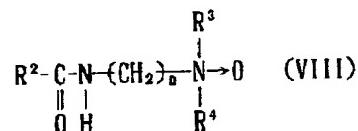
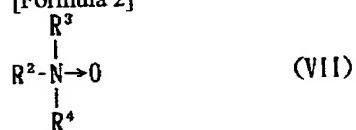


[0022] (R2 shows the alkyl or alkenyl machine of carbon numbers 8-22 among a formula, R3 and R4 show independently the alkyl group of carbon numbers 1-3, respectively, A shows a hydrogen atom or a hydroxyl group, B shows -COO- or -SO₃-, and n shows the integer of 1-5.)

Moreover, as an amine oxide system surfactant used for this invention, it is the following general formula (VII). Or (VIII) the tertiary amine oxide expressed is mentioned.

[0023]

[Formula 2]

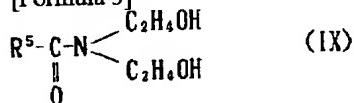


[0024] (R2, R3, and R4 and n show the aforementioned meaning among a formula.)

Moreover, as a fatty-acid diethanolamide system surfactant used for this invention, the compound expressed with the following general formula (IX) is mentioned.

[0025]

[Formula 3]



[0026] (R5CO- shows the saturation or the unsaturated fatty acid residue of carbon numbers 10-20 among a formula.)

It sets to a general formula (IX) and is R5CO. - As a fatty-acid residue shown, the residue of fatty acids, such as a lauric acid, a myristic acid, a palmitic acid, oleic acid, stearin acid, isostearic acid, palm oil fatty acid, a palm-kernel-oil fatty acid, a beef tallow fatty acid, a castor oil fatty acid, and a rapeseed-oil fatty acid, is mentioned, and a lauric acid, palm oil fatty acid, and a palm-kernel-oil fatty acid are desirable in these.

- [0027] (c) in the cleaning agent constituent of this invention The content of a component has 0.1 - 10 desirable % of the weight, and its 1 - 8 % of the weight is still more desirable.
 - [0028] Although the remainder of the aforementioned component of the cleaning agent constituent of this invention is water, nonionic surface active agents, such as fatty acid alkanolamide other than a sulfate type or anionic surface active agents other than sulfonate type anion surface activity, and fatty-acid diethanolamide, can be included. Furthermore, low-grade alkylbenzene sulfonates, such as glycols, such as lower alcohols like a well-known low-temperature stabilizer, for example, ethanol, and an isopropanol before, ethylene glycol, a polyethylene glycol, a propylene glycol, and a polypropylene glycol, a benzenesulfonic-acid salt, a p-toluenesulfonic-acid salt, and a xylene sulfonate, acetamides, and the aromatic carboxylates like a benzoate or a salicyte salt, a hand dry-area inhibitor, an enzyme, a germicide, an antimicrobial agent, a protein derivative, opaquer, a colorant, preservatives, perfume, a bleaching agent, a rust-proofer, and a chelating agent, are mentioned to the organic builder and the inorganic builder for raising the detergency of a citric acid, a malic acid, a gluconic acid, or its salt, and a pan.
 - [0029] Although the cleaning agent constituent of this invention is suitably used as hard surface washing agents, such as a cleaning agent for kitchens, a cleaning agent for dwellings, and metal plastics, the cleaning agent for garments, the cleaning agent for hair, a cleaning agent for the bodies, etc., it is desirable to use as a cleaning agent for kitchens especially.
-

[Translation done.]

*** NOTICES ***

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Following (a) A component and (b) A component and (c) Liquid cleaning agent constituent characterized by containing a component.

(a) Compound RO-(EO)x-(PO)y-(EO)x' expressed with a general formula (I) - H (I)
R shows the alkyl group or ARUKENIRU machine of the straight chain of carbon numbers 8-22, or branched chain among [formula, EO shows an oxyethylene machine and PO shows an oxypropylene machine. x and x' is one or more numbers which show the number of average addition mols of an ethyleneoxide, and the sums of x and x' are 4-20. y It is the number of 0.5-6 which shows the number of average addition mols of ** propylene oxide. In addition, x, (PO)y, and (EO)x' are carrying out block combination at this order.]

(b) A sulfate type or sulfonate type anionic surface active agent (c) An amphoteric surface active agent, an amine oxide system surfactant, or fatty-acid diethanolamide system surfactant. [Claim 2] (a) The content of a component is 0.5 - 20 % of the weight, and (b). The content of a component is 1 - 50 % of the weight, and (c). Liquid cleaning agent constituent according to claim 1 whose content of a component is 0.1 - 10 % of the weight.

[Claim 3] The liquid cleaning agent constituent according to claim 1 or 2 which is an object for kitchens.

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CLIPPEDIMAGE= JP411012594A
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DOCUMENT-IDENTIFIER: JP 11012594 A
TITLE: LIQUID CLEANER COMPOSITION

PUBN-DATE: January 19, 1999

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ASSIGNEE-INFORMATION:

NAME	COUNTRY
KAO CORP	N/A

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C11D001/52
; C11D001/75 ; C11D001/83 ; C11D001/835 ; C11D001/90 ; C11D001/92
; C11D001/94

ABSTRACT:

PROBLEM TO BE SOLVED: To obtain a liquid cleaner composition excellent in foaming force, activities for lowering the oil/water interface tension while maintaining the low temperature stability excellent.

SOLUTION: This liquid cleaner composition comprises (a) 0.5-20 wt.% compound of the formula; RO-(EO)<SB>x</SB>-(PO)<SB>y</SB>-(EO)<SB>x</SB>' -H [R is an 8-22C alkyl group, etc.; EO is an oxyethylene group; PO is an oxypropylene group; (x) and (x') are each a number of ≥1, with the proviso that the sum of (x) and (x') is 4-20; (y) is a number of 0.5-6; with the proviso that (EO)<SB>x</SB>, (PO)<SB>y</SB>, and (EO)<SB>x</SB>', forms block bonds in the order], (b) 1-50 wt.% sulfate type or sulfonate type anionic surfactant and, (c) 0.1-10 wt.% amphotolytic, amine oxide-based or fatty acid diethanolamide-based surfactant.

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(54)【発明の名称】 液体洗浄剤組成物

(57)【要約】

【課題】 低温安定性を良好に維持したまま、起泡力及び油／水界面張力低下能に優れる液体洗浄剤組成物の提供。

【解決手段】 (a)一般式(I)で表される化合物、
(b) サルフェート型あるいはスルホネート型アニオン界面活性剤、及び(c)両性界面活性剤、アミンオキサイド系界面活性剤又は脂肪酸ジエタノールアミド系界面活性剤を含有する液体洗浄剤組成物。

RO-(EO)_x-(PO)_y-(EO)_{x'}-H (I)

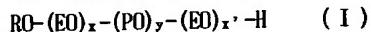
[式中、Rは炭素数8~22のアルキル基等、EOはオキシエチレン基、POはオキシプロピレン基、x, x'は1以上の数で、xとx'の和は4~20、yは0.5~6の数である。尚、(EO)_x、(PO)_y、(EO)_{x'}はこの順にブロック結合している。]

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【特許請求の範囲】

【請求項1】 下記(a)成分、(b)成分及び(c)成分を含有することを特徴とする液体洗浄剤組成物。

(a) 一般式(I)で表される化合物



[式中、Rは炭素数8~22の直鎖又は分岐鎖のアルキル基又はアルケニル基を示し、EOはオキシエチレン基、POはオキシプロピレン基を示す。x、x'はエチレンオキサイドの平均付加モル数を示す1以上の数で、xとx'の和は4~20である。yはプロピレンオキサイドの平均付加モル数を示す0.5~6の数である。尚、(EO)_x、(PO)_y、(EO)_zはこの順にブロック結合している。]

(b) サルフェート型あるいはスルホネート型アニオン界面活性剤

(c) 両性界面活性剤、アミンオキサイド系界面活性剤又は脂肪酸ジエタノールアミド系界面活性剤

【請求項2】 (a) 成分の含有量が0.5~20重量%、

(b) 成分の含有量が1~50重量%、(c) 成分の含有量が0.1~10重量%である請求項1記載の液体洗浄剤組成物。

【請求項3】 台所用である請求項1又は2記載の液体洗浄剤組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は液体洗浄剤組成物に関し、詳しくは低温安定性を良好に維持したまま、起泡力及び油/水界面張力低下能に優れる液体洗浄剤組成物に関するものである。

【0002】

【従来の技術及び発明が解決しようとする課題】家庭用の洗浄剤組成物に求められる最も基本的な性能として洗浄力と起泡力が挙げられる。一般に洗浄力と起泡力との間に普遍的な関連性はないと言われている。しかしながら、消費者は洗浄時に泡の消失をもって洗浄力を判断することが多く、また嗜好性の点からも豊かな泡立ちを好む傾向にある。この為、商品としては起泡力、特に油汚れ存在下でも豊かな泡立ちを持つ洗浄剤が好ましい。

【0003】従来の洗浄剤は、主に起泡力の理由からアニオン界面活性剤を主洗浄基剤とし、更に油汚れ存在下での起泡力増強、皮膚に対する作用の緩和といった目的で、第3級アミンオキサイド、高級脂肪酸アルカノールアミド、アルキルベタイン等の含窒素両性、カチオン性又は非イオン性界面活性剤が併用されている。しかしながら、これら界面活性剤の組み合わせによる洗浄剤組成物では、一般的に界面活性剤の界面化学的性質上、油脂汚れに対する乳化力が高くなる程、起泡力が損なわれる傾向にある。

【0004】また、サルフェート型あるいはスルホネート型アニオン界面活性剤は、優れた洗浄力及び起泡力を持った界面活性剤であり、液体洗浄剤の原料として広く

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用いられてきた。しかしながら、配合物の低温安定性が悪いため、低温安定化剤として、エタノール等の低級アルコール類、ベンゼンスルホン酸塩やp-トルエンスルホン酸塩等の低級アルキルベンゼンスルホン酸塩、エチレングリコールやプロピレングリコール等のグリコール類、尿素等が単独又は組み合わせて使用されてきた。これらの中で尿素は優れた効果を示し且つ経済的であるために広く用いられているが、高温で保存した場合に分解してアンモニア臭等の不快臭を発生したり、pHを上昇させたりする欠点がある。一方、その他の低温安定化剤は、少量では効果が少なく、多量配合しても充分な低温安定化効果は認められず、且つ不経済である。

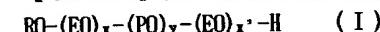
【0005】そこで、界面活性剤として洗浄力をもち、且つ低温安定化効果のあるアルコールエトキシレート系非イオン界面活性剤と併用することが試みられてきたが、低温安定化効果は未だ充分でなく多量に配合すると洗浄性、起泡性も低下する欠点があった。

【0006】従って、本発明の目的は、低温安定性を良好に維持したまま、起泡力及び油/水界面張力低下能に優れる洗浄剤組成物を提供することにある。

【0007】

【課題を解決するための手段】本発明者らは銳意研究を行った結果、特定のアルキレンオキサイド付加モル数及び付加形態を持つ三元ブロック共重合体を配合することにより上記課題が解決できることを見出し本発明を完成するに至った。即ち、本発明は、下記(a)成分、(b)成分及び(c)成分を含有することを特徴とする液体洗浄剤組成物を提供するものである。

【0008】(a) 一般式(I)で表される化合物



[式中、Rは炭素数8~22の直鎖又は分岐鎖のアルキル基又はアルケニル基を示し、EOはオキシエチレン基、POはオキシプロピレン基を示す。x、x'はエチレンオキサイドの平均付加モル数を示す1以上の数で、xとx'の和は4~20である。yはプロピレンオキサイドの平均付加モル数を示す0.5~6の数である。尚、(EO)_x、(PO)_y、(EO)_zはこの順にブロック結合している。]

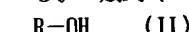
(b) サルフェート型あるいはスルホネート型アニオン界面活性剤

(c) 両性界面活性剤、アミンオキサイド系界面活性剤又は脂肪酸ジエタノールアミド系界面活性剤

【0009】

【発明の実施の形態】以下、本発明の実施の形態を詳細に説明する。

【0010】[(a)成分] 本発明の洗浄剤組成物は、(a)成分として上記一般式(I)で表される化合物を含有する。一般式(I)で表される化合物は、一般式(II)



(式中、Rは前記の意味を示す。)で表されるアルコールにエチレンオキサイド、次にプロピレンオキサイド、

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更にエチレンオキサイドを順にブロック付加させることにより得ることができる。

【0011】一般式(II)で表されるアルコールとしては、炭素数8~22、好ましくは10~14の飽和もしくは不飽和の1級もしくは2級の直鎖又は分枝鎖のアルコールが挙げられ、具体的な例としては、デシルアルコール、ラウリルアルコール、ミリストルアルコール、ステアリルアルコール等の直鎖アルコール、炭素数8~22の範囲で混合された混合アルコール、オキソ法やチーグラー法を用いて合成された分枝を有する炭素数8~22のアルコール等が挙げられ、特にラウリルアルコールが好ましい。

【0012】また、これらのアルコールにアルキレンオキサイドを付加する方法としては、公知のアルコキシリ化方法を用いて、触媒の存在下付加する方法が挙げられるが、アルキレンオキサイドの付加順序は、まずエチレンオキサイドを付加し、次にプロピレンオキサイドを付加し、さらにエチレンオキサイドを順にブロック付加する必要がある。エチレンオキサイド、プロピレンオキサイドをランダムに付加させたものだと、泡立ちが阻害されてしまい好ましくない。

【0013】本発明の一般式(I)で表される化合物のエチレンオキサイドの平均付加モル数の合計($x+x'$)は4モル以上20モル以下であり、好ましくは5モル以上8モル以下である。エチレンオキサイドの平均付加モル数の合計が4モル未満であると、一般式(I)で表される化合物と水との相溶性が悪くなり、また20モルを超えるとハンドリング性が悪くなる。

【0014】また、一般式(I)で表される化合物のプロピレンオキサイドの平均付加モル数 y は、0.5モル以上6モル以下であり、2モル以上4モル以下が好ましく、特に2モルが好ましい。プロピレンオキサイドの平均付加モル数が0.5モルに満たない場合には、粘度の変化が大きくハンドリング性が悪化し、6モルを越える量を付加すると、洗浄力が低下する。

【0015】本発明の洗浄剤組成物中の(a)成分の含有量は0.5~20重量%が好ましく、1~10重量%が更に好ましい。

【0016】[(b)成分] 本発明の洗浄剤組成物は(b)成分として、サルフェート型あるいはスルホネート型アニオン界面活性剤を含有する。本発明に用いられるサルフェート型あるいはスルホネート型アニオン界面活性剤としては、例えば、下記の(i)~(v)の群から選ばれる1種又は2種以上が挙げられる。

【0017】(i) アルキル基の炭素数が9~15、好ましくは11~14、特に好ましくは12の直鎖アルキルベンゼンスルホン酸塩

(ii) 炭素数8~22、好ましくは12~16のアルコールを硫酸化することによって得られるアルキル硫酸塩

(iii) 炭素数8~22、好ましくは12~16のアルカンスル

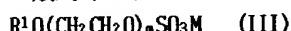
ホン酸塩

(iv) 炭素数8~22、好ましくは12~16の α -オレフィンスルホン酸塩

(v) 炭素数8~22、好ましくは12~16のアルコールをエチレンオキサイド1~30モル、好ましくは1~12モルでエトキシ化することによって誘導されるポリオキシエチレンアルキルエーテル硫酸塩

これらの(b)成分のうち、洗浄力及び皮膚温和性の点でポリオキシエチレンアルキルエーテル硫酸塩、特に次の

10 一般式(III)



(式中、 R^1 は炭素数12~16のアルキル基、又はアルケニル基を、Mはアルカリ金属、アンモニウム又はアルカノールアミンを示し、 n は平均で1~12の数を示す。)で表されるポリオキシエチレンアルキルエーテル硫酸塩が好ましい。

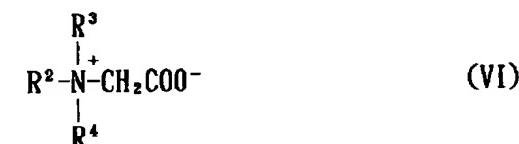
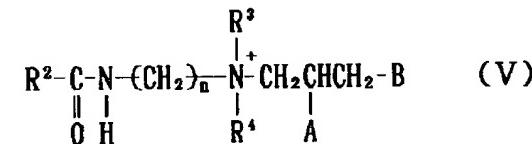
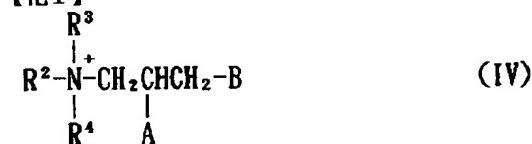
【0018】本発明の洗浄剤組成物中の(b)成分の含有量は1~50重量%が好ましく、5~30重量%が更に好ましい。

20 20 一般式(IV) [(c)成分] 本発明の洗浄剤組成物は、起泡力を向上させ、皮膚に対する作用を改善させるために、(c)成分として両性界面活性剤、アミンオキサイド系界面活性剤又は脂肪酸ジエタノールアミド系界面活性剤を含有する。

【0020】本発明に用いられる両性界面活性剤としては、下記一般式(IV)~(VI)で表されるアルキルカルボベタイン及びアルキルスルホベタインが挙げられる。

【0021】

【化1】



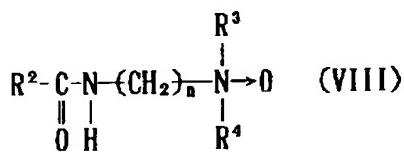
【0022】(式中、 R^2 は炭素数8~22のアルキル又はアルケニル基を示し、 R^3 及び R^4 はそれぞれ独立して炭素数1~3のアルキル基を示し、Aは水素原子又は水酸基を示し、Bは $-COO^-$ 又は $-SO_3^-$ を示し、nは1~5の整数を示す。)

5

また、本発明に用いられるアミンオキサイド系界面活性剤としては、下記一般式(VII)又は(VIII)で表される第3級アミンオキサイドが挙げられる。

【0023】

【化2】

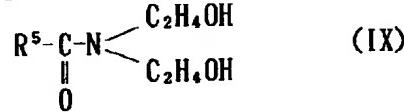


【0024】(式中、 R^2 、 R^3 、 R^4 及び n は前記の意味を示す。)

また、本発明に用いられる脂肪酸ジエタノールアミド系界面活性剤としては、下記一般式(IX)で表される化合物が挙げられる。

【0025】

【化3】



【0026】(式中、 $\text{R}^5\text{CO}-$ は炭素数10~20の飽和又は不饱和脂肪酸残基を示す。)

一般式(IX)において、 $\text{R}^5\text{CO}-$ で示される脂肪酸残基としては、ラウリン酸、ミリスチン酸、パルミチン酸、オレイン酸、ステアリン酸、イソステアリン酸、ヤシ油脂肪酸、パーム核油脂肪酸、牛脂脂肪酸、ひまし油脂肪酸、ナタネ油脂肪酸等の脂肪酸の残基が挙げられ、これらの中ではラウリン酸、ヤシ油脂肪酸、パーム核油脂肪酸が好ましい。

【0027】本発明の洗浄剤組成物中の(c)成分の含有量は0.1~10重量%が好ましく、1~8重量%が更に好ましい。

【0028】本発明の洗浄剤組成物の前記成分の残部は水であるが、その他に、サルフェート型あるいはスルホネット型アニオン界面活性以外のアニオン界面活性剤、脂肪酸ジエタノールアミド以外の脂肪酸アルカノールアミド等のノニオン界面活性剤を含むことができる。さらに、従来公知の低温安定剤、例えば、エタノール、イソプロパノールのような低級アルコール類、エチレングリコール、ポリエチレングリコール、プロピレングリコール、ポリプロピレングリコール等のグリコール類、ベンゼンスルホン酸塩、p-トルエンスルホン酸塩、キシリソスルホン酸塩等の低級アルキルベンゼンスルホン酸塩

6

類、アセトアミド類、安息香酸塩やサリチル酸塩のような芳香族カルボン酸塩類などを併用することができる。その他液体洗浄剤に配合できるものとして既に公知の諸物質をその目的に応じて適宜併用できる。このような物質としては、クエン酸、リンゴ酸、グルコン酸又はその塩等の洗浄力を向上させるための有機ビルダーや無機ビルダー、さらに手荒れ防止剤、酵素、殺菌剤、抗菌剤、蛋白質誘導体、不透明化剤、着色料、保存料、香料、漂白剤、防錆剤、キレート剤等の添加物が挙げられる。

10 【0029】本発明の洗浄剤組成物は、台所用洗浄剤、住居用洗浄剤、金属プラスチック等の硬質表面洗浄剤、衣料用洗浄剤、毛髪用洗浄剤、身体用洗浄剤等として好適に用いられるが、特に台所用洗浄剤として用いるのが好ましい。

【0030】

【実施例】以下、実施例を挙げて本発明の洗浄剤組成物を更に詳しく説明するが、本発明はこれらの実施例に限定されるものではない。例中の部及び%は特記しない限り重量基準である。

20 【0031】なお、実施例で用いた(a)成分は、下記の条件下で、それぞれのエチレンオキサイド又はプロピレンオキサイドの付加モル数に応じて添加量を変えることによって合成した。合成条件を以下に示す。エチレンオキサイド用とプロピレンオキサイド用の2つの計量槽の付いた5m³の回転攪拌式オートクレーブ中にラウリルアルコール〔「商品名カルコール2098」、花王(株)製〕を500g、水酸化カリウムを3.0g仕込み、窒素置換を行った後110℃に昇温し、40torrで1時間脱水を行った。次に150℃に昇温し、目的の化合物に対応する量のエチレンオキサイド〔一般式(I)のxにあたる量〕を3.5kg/m²の圧力でオートクレーブ中に導入し、圧力が低下して一定になるまで反応させたのち、120℃に冷却して目的の化合物に対応する量のプロピレンオキサイド〔一般式(I)のyにあたる量〕をオートクレーブ中に3.5kg/m²の圧力で導入し、圧力が低下して一定になるまで反応させた。その後、再び150℃に昇温しエチレンオキサイド〔一般式(I)のx'にあたる量〕を3.5kg/m²の圧力でオートクレーブ中に導入し、圧力が低下して一定になるまで反応させ、反応終了後、温度を低下させ、酢酸3.2gを添加し中和することで、目的の最終の生成物を得た。

【0032】実施例1~6及び比較例1~4

表1及び表2に示すベース配合物を調製し、このベース配合物に表1及び表2に示す(a)成分又は(a')成分を表1及び表2に示す割合で添加して洗浄剤組成物を調製した。得られた洗浄剤組成物について下記方法により油/水界面張力低下効果、増泡効果、クラフト点低下効果及び油汚れ洗浄力を評価した。結果を表1及び表2に示す。

50 【0033】<油/水界面張力低下効果>各組成物を40

倍に水で希釈した液と水との界面の界面張力をWilhelmy平板法により測定し(25°C)、下記基準で効果を判定した。なお、ベース配合物を40倍に水で希釈した液での値を基準値とした。

判定基準

+ : 各組成物での測定値が基準値よりも低い

± : 各組成物での測定値が基準値と変わらない

- : 各組成物での測定値が基準値よりも高い。

【0034】<増泡効果>洗浄剤組成物濃度 0.2%の洗剤溶液(使用水はドライ硬度 3.5° DH の水) 40mlを直径5cmのガラス円筒に入れ、回転羽根で攪拌した後、泡高さを測定し、下記基準で判定した。なお、ベース配合物での値を基準値とした。

判定基準

+ : 各組成物での測定値が基準値よりも高い

± : 各組成物での測定値が基準値と変わらない

* - : 各組成物での測定値が基準値よりも低い。

【0035】<クラフト点低下効果>各組成物のクラフト点を測定し、下記基準にて効果を判定した。なお、ベース配合物での値を基準値とした。

判定基準

+ : 各組成物での測定値が基準値よりも低い

± : 各組成物での測定値が基準値と変わらない

- : 各組成物での測定値が基準値よりも高い

<油汚れ洗浄力>牛脂に指示薬としてスタンIII(赤色色素)を0.1%添加し、この2.5gを磁製の皿(直径25cm)に塗布した。これを、洗浄剤組成物3gを水(硬度3.5° DH)27gに溶解した溶液をしみ込ませたスポンジを用いて液温20°Cでこすり洗いし、牛脂が十分に洗浄・除去できた皿の枚数をもって洗浄力を表した。

【0036】

【表1】

		実施例					
		1	2	3	4	5	6
液体洗浄剤組成物	オクタキシエチレン(E0=3)ラウリルエーテルカクテート	18	18	18		18	15
	α-オレフィン(C ₁₄)スルホネート				12		
	ラウリルジメチルアミノオキサイド	7	7	7	3		
	N-(3-アクリルアミドプロピル)-N-ジメチルモニオカルボキシペタイン					3	
	バーム接油脂肪酸ジエタノールアミド						7
	エタノール	5	5	5	5	5	5
	イオン交換水	65	65	65	75	69	68
	R=C ₁₂ H ₂₅ x=2, y=2, x'=3	5					5
	(a) 成分 [*] R=C ₁₂ H ₂₅ x=3, y=2, x'=3		5		5		
	R=C ₁₂ H ₂₅ x=2, y=2, x'=5			5		5	
(部)	(a') 成分 ^{**} R=C ₁₂ H ₂₅ x=0, y=2, x'=3						
	R=C ₁₂ H ₂₅ x=0, y=0, x'=6						
pH		7	7	7	7	7	7
評価結果	油／水界面強力低下効果	+	+	+	+	+	+
	増泡効果	+	+	+	+	+	+
	クラフト点低下効果	+	+	+	+	+	+
	油汚れ洗浄力 (枚数)	10	10	10	9	9	9

※ ※ 【表2】

【0037】

9

10

		比 較 例				
		1	2	3	4	
液 体 洗 净 剂 組 成 物 (部)	ベ ン ス 配 合 物	ポリオキシエチレン(B0=3)ラウリルエーテルソルブエート $R=C_{12}H_{25}$ $x=2, y=2, x'=3$	18	18		18
		α -オレフィン(C_{14})スルホネート				
		ラウリルジメチルアミノキサイド	7	7	3	
		N-(3-ドテカノイルアミドプロピル)-N,N-ブチル アンモニオカルボキシペタイン				
		バーム核油脂脂肪酸ジエタノールアミド				
		エタノール	5	5	5	5
		イオン交換水	65	65	87	72
(a) 成分 ^{*1} (a') 成分 ^{*2}	$R=C_{12}H_{25}$ $x=2, y=2, x'=3$					
	$R=C_{12}H_{25}$ $x=3, y=2, x'=3$			5		
	$R=C_{12}H_{25}$ $x=2, y=2, x'=5$				5	
	$R=C_{12}H_{25}$ $x=0, y=2, x'=3$	5				
	$R=C_{12}H_{25}$ $x=0, y=0, x'=6$		5			
	pH		7	7	7	7
評 価 結 果	油／水界面張力低下効果	+	-	-	-	
	増泡効果	-	+	-	-	
	クラフト点低下効果	+	+	+	+	
	油汚れ洗浄力 (枚数)	7	7	2	3	

【0038】注)

30 * 【0039】*2 : (a) 成分の比較品、一般式(I)で表

*1: 一般式(I)で表される化合物中のR, x, y, x' の値で示す。
 値で示す。
 *2: (a') 成分の比較品、一般式(I)で表される化合物中のR, x, y, x' の値で示す。

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